



**Purpose:**

EDTA Titration Method E3000A.  
Determination Of Manganese In Organo-Manganese Compounds.

**Scope:**

This procedure describes the determination of the percent manganese by volumetric titration.

**Safety:**

The analyst should wear chemical resistant gloves and safety glasses to prevent all skin and eye contact.

Ammonium hydroxide (NH<sub>4</sub>OH) may cause severe burns if contacted by the skin or eyes. It may be fatal if inhaled through pneumonitis or pulmonary edema (the filling of the lungs with water). If swallowed, it is extremely corrosive to the respiratory and digestive systems.

Ammonium chloride may cause irritation of the mouth, nose and throat and may cause wheezing, chest pain, and delayed pulmonary edema..

Bromine is corrosive and toxic and should be handled only in a well-ventilated hood. Inhalation of small amounts causes copious mucous secretion, coughing, nosebleed, a feeling of oppression, vertigo, dizziness, headache, nausea, diarrhea, stomach pain, hoarseness, and respiratory difficulty. Inhalation of high concentrations results in inflamed lesions of the mucous membranes or the upper respiratory tract, and fatal chemical burns of the lungs. The tongue and palate will appear inflamed and swollen. There will be glottal spasms, and asthmatic spasms of the bronchi. Expelled air will have a very characteristic odor. Resulting pulmonary edema and chemical pneumonitis may be delayed for several hours. Prolonged or repeated exposure to bromine concentrations of < 0.1 mg/ml may cause headache, chest pains, anorexia, indigestion, irritation and joint pain. Exposure for 5-6 years at this level may result in loss of corneal reflexes, pharyngitis, thyroid dysfunction, cardiovascular disorders, disorders of the secretory function of the digestive tract, and may deposit and accumulate in the tissues causing central nervous system damage. An exposure of 3.5 ppm is detectable. 10 ppm is severely irritating. 40-60 ppm is dangerous, even for brief periods of time, and 1000 ppm is fatal.

Chloroform is extremely hazardous and should be handled only in a well-ventilated hood. It is a known carcinogen and an irritant of the eyes and the mucous membranes of the upper respiratory tract. It may be fatal if swallowed, inhaled, or absorbed through the skin. Exposure may cause nausea, dizziness, and headache. Chronic effects include damage to the liver, kidneys, heart and possible alteration of genetic material causing mutations.

EDTA (Versene) is moderately toxic by ingestion. It is a moderate irritant of the skin and eyes and may cause slight burns if contacted. It may cause conjunctivitis if contacted by the eyes.

Hydrochloric acid (HCL) will cause pain, irritation, and possible permanent reduction or loss of vision if in contact with the eyes. Concentrated acid or gas can cause severe burns if in contact with the skin. Inhalation of HCl gas can cause irritation and damage to the tissues of the nose, throat, and lungs

Hydroxylamine hydrochloride is harmful if swallowed, inhaled, or absorbed through the skin. It is destructive to the tissues of the mucous membranes, upper respiratory tract, eyes and skin. Inhalation may be fatal by spasm, inflammation and edema of the larynx and bronchi, chemical pneumonitis. and pulmonary edema. Symptoms of overexposure include a burning sensation, coughing, wheezing, laryngitis, headache, nausea, and vomiting.



Organo-manganese compounds are toxic. Samples must be handled in a well-ventilated hood. The analyst must wear safety glasses-, rubber gloves, and protective clothing. Spill pans should be placed below equipments in which the compound is handled.

**Outline of Method:**

The sample is dissolved in chloroform and treated with bromine and with hydrochloric acid to decompose the organo-manganese compound. The bromine is expelled by boiling and the residual excess removed with hydroxylamine hydrochloride. The pH of the aqueous phase is adjusted with ammonium chloride and hydrochloric acid, and the manganese is titrated with EDTA (Versene) using calmagite indicator.

**Apparatus:**

1. Beaker: tall-form. 400 ml capacity
2. Buret: automatic delivery. 50 ml capacity with 0.1 ml subdivisions
3. Magnetic stirrer and stirring bar
4. Hotplate: Corning Model PC\_500 with glass ceramic top, or equivalent
5. Disposable Hypodermic Syringe: with scabbard. 3.0 ml capacity with 1 1/2 in No. 22 gauge needle

**Reagents:**

1. Ammonium Chloride 20% Solution: Dissolve 80 g of ammonium chloride in 400 ml of deionized water.
2. Bromine: reagent grade.
3. Chloroform: reagent grade.
4. Calmagite Indicator Solution: Dissolve 1.5 g of 1-(1-hydroxy-4-methyl-2-phenylazo)-2-naphthol-4-sulfonic acid in 600 ml of deionized water.
5. Calmagite Indicator: 1-(1-hydroxy-4-methyl-2-phenylazo)-2-naphthol-4-sulfonic acid. Eastman Organic Chemicals No. 8254, or equivalent.
6. Ethylenediaminetetraacetic Acid (EDTA) or Versene: approximately 0.1M, Dissolve 37.2200 g of disodium dihydrogen ethylenediamine-tetraacetate dihydrate in distilled water or purchase 0.1 M solution. (1 ml is equivalent to 5.493 mg of Mn).
7. Hydrochloric Acid, dilute: Add 800 ml of concentrated hydrochloric acid to 15,200 ml of deionized water.
8. Hydroxylamine Hydrochloride Solution: Dissolve 40 g of hydroxylamine hydrochloride in 400 ml of deionized water.
9. Hydroxylamine Hydrochloride: reagent grade
10. Methyl Red Indicator Solution: Dissolve 0.5 g of water-soluble methyl red in 500 ml of deionized water.
11. Methyl Red Indicator: reagent grade.

**Procedure:**

1. Place the sample-jar in an exhaust hood. Remove the sample jar cap and, using a 3.0 ml disposable syringe, withdraw 0.5 ml of sample for manganese analyses. Withdraw the syringe

needle from the sample and wipe dry with an absorbent tissue. Place a rubber stopper on the tip of the syringe needle. Replace the sample jar can.

2. Place the syringe containing the sample on an analytical balance and tare. Inject the contents of the syringe into a tall-form, 400 ml beaker. The beaker should be in an exhaust hood and should contain a magnetic stirring bar. Replace the syringe on the analytical balance and read the weight of sample used. Record the sample weight to  $\pm 0.0001$  g.
3. Add 33 ml of chloroform, 1.5 ml of bromine, and 50 ml of dilute hydrochloric acid to the solution in the beaker. Boil the solution gently for a few moments to expel most of the bromine (no longer elutes reddish-brown fumes). Remove from the hotplate and cool the solution to room temperature.
4. Add 2.5 ml of hydroxylamine hydrochloride solution, 5 ml of ammonium chloride solution, and 4 drops of methyl red indicator solution. Add concentrated ammonium hydroxide DROPSWISE until the solution turns yellow (or until the red disappears) and then add 8 ml of the ammonium hydroxide into the sample solution.
5. Add 4 ml of calmagite solution to give a definite "cherry red" color.
6. Titrate with 0.1M EDTA (Versene) solution until the color changes to a cobalt blue
7. Calculate the percent manganese as follows (see worksheet below):

$$\text{ml(Versene)} \times F(\text{Versene}) = \% \text{ Mn sample weight (mg)}$$

Where F = factor for EDTA (in mg Mn/ml solution) with 5.493 mg Manganese per ml 1.000 M EDTA When using a 0.1005 M EDTA solution,  $F = (0.1005 \text{ M}) \times (5.493 \text{ mg Mn/ml } 1.0 \text{ M EDTA}) = 0.5520$ .

8. Clean the glassware by washing with acetone, then a small amount of HCl/H<sub>2</sub>O (if needed to remove stubborn residue), and hot, soapy water. Rinse with acetone and dry.
9. Record the results of the analysis on the form below.



**Manganese Analysis Log and Calculation Sheet:**

Sample Description		
Manufacturer ID		
Batch / Lot		
Test Date		
Analyst		
Sample Weight (grams)		S
EDTA concentration (molarity)		C
EDTA titrant volume (ml)		V
Calculate EDTA Factor:		$F = C * 5.493$
Calculate wt% Manganese:		$M = \frac{V \times F}{S}$

**Specifications:**

	Wt% Manganese (min)
Ecotane® 3062	15.1
Ecotane® 3000	24.4

**QC Status:**

Approved       Rejected

**Certification:**

I certify that the above results are correct and accurate.

Signature: \_\_\_\_\_ Date: \_\_\_\_\_

